AVAILABILITY OF AEROSPACE RAYON FOR SRM NOZZLE INSULATORS

R. C. Rossi
Strategic Systems Division, TRW Inc.
San Bernardino, CA
and
W. C. Wong
Space Technology Division, TRW Inc.
Redondo Beach, CA

ABSTRACT

For approximately 30 years, the nozzles of solid rocket motors (SRM) have used an aerospace grade of rayon as a precursor for carbon fabric reinforcement in phenolic composites employed as ablative insulators. Rayon has been the industry mainstay ever since and modern nozzle designs have been dependent upon the properties of carbon, fabric/phenolic, or graphite fabric/phenolic composites derived from this material. Over the years, the industry has been dependent upon a sole source supplier. The present supplier, North American Rayon Corporation, is the last surviving rayon manufacturer in the country. Like many aerospace suppliers, it has been affected by cutbacks in defense procurement and is planning to discontinue the production of the aerospace grade rayon. At this time, production is continuing on back orders for life-of-type buys. These orders will be completed by the end of 1996 at which time the domestic source for continuous filament rayon will disappear.

Alternatives to rayon have been evaluated as a carbon fabric precursor; however, the poor performance of demonstration hardware using these materials has revealed that none of these alternatives represent a drop-in replacement. The continuing availability of rayon for aerospace applications is now being studied by a joint NASA/DoD team.

BACKGROUND

For more than 30 years, nozzle insulator components have been made from a phenolic resin composite reinforced with carbon or graphite fabric. These reinforcing materials are made from rayon fabric through a thermal conversion process. Their use in nozzle components imparts unique combinations of properties that have not been surpassed in spite of many advanced material developments during recent years. Carbon and graphite fabric replaced silica and glass fiber fabric in nozzle components because they offered increased thermal resistance, lower erosion, and 20% weight reduction. Without the rayon-based carbon/graphite phenolic composites, the solid rocket motors now used in ballistic, launch, and shuttle boost vehicles would not be possible. These materials allow for larger motors having long burn times and hotter propellants. Design, performance, and weight requirements established in the use of rayon-based fabric reinforcement are compromised when substituted by all candidate replacement materials.

Whereas the importance of rayon to the SRM industry is well established, the source of the rayon has not been as certain. The aerospace grade rayon has always been obtained from a sole source vendor. Over the years, several different vendor sources have been used (Table 1). At the time rayon-based reinforcements were introduced into the SRM industry, rayon fiber production was a large business with rayon used in clothing fabric, sewing thread, and tire cord reinforcement. Over the years, polyester fiber has replaced rayon in all these major commercial

Table 1. Production Chronology of Aerospace Rayon[1]

Year	Activity
1940	Courtaulds builds Front Royal, VA plant
1964	IRC-American Cynamid produces first aerospace grade rayon yarns
1972	American ENKA produces aerospace rayon yarns
1975	American Viscose-FMC produces aerospace rayon yarns
1976	AVTEX Fibers, Inc. purchases FMC Front Royal, VA plant and continues aerospace rayon production
1988	AVTEX Fibers, Inc. closes Front Royal plant
1988	DoD and NASA provide $44M to re-open AVTEX Front Royal plant (6-month production)
1988	NASA starts development of alternative source (North American Rayon Corp.)
1989	AVTEX Fibers, Inc. closes Front Royal plant
1990	NARC becomes sole source producer of rayon yarn in Elizabethon, TN
1996	NARC closure planned by year's end

uses for this material. In the early years (1965-1970), aerospace grade rayon represented a minuscule share of the market and justified a sole source vendor. In 1996, a reduced aerospace demand represented 10% of the domestically produced continuous filament rayon fiber.

In 1989, Avtex, the sole vendor for aerospace grade rayon, was forced to shut down because it could not meet state clean water regulations. The aerospace grade rayon vendor status was transferred to the North American Rayon Corporation (NARC), the sole remaining producer of continuous filament rayon fiber in the U.S. In May of this year, NARC informed the aerospace industry that it too will shut down because: 1) it lost a major share of its commercial market to foreign competition and 2) aerospace orders were not able to meet production requirements and the business could not afford to produce inventory for an uncertain market.

The aerospace industry responded by generating life-of-type buys for 2.5M pounds of rayon fiber within two months of this notice. These orders represent more than four years of production at prior production rates, but because commercial fiber production can now be converted to aerospace grade, the orders will be filled before the end of this calendar year. Nearly every major existing SRM program had responded so as to protect itself, even those that have not yet received production contracts. A need for a new rayon fiber source may have been put off as much as five years.

WHY RAYON FIBERS?

Among the many synthetic fibers available on the market, most of them oil-based, it isn't at all apparent why rayon, the oldest synthetic fiber, should produce a carbonizable fiber with superior properties for nozzle components. Rayon is made from a cellulose acetate viscose by a process that by today's standards might be considered to be low-technology. Figure 1 is a process flow schematic that defines process steps and identifies chemical reactions. The manufacture of rayon fiber is normally done in a continuous process, where control of rayon type is attained by resident time and flow rates through the sequential process tanks. The aerospace grade is intermediate in processing conditions between the stronger commercial fiber used for tire cord reinforcement and the lower strength, high-sheen grade used in fabrics.

The relationship among rayon grades and properties is shown in Figure 2. A major requirement of the aerospace grade is that, when carbonized, it must produce a fiber with a crenulated cross-section. This cross-section is credited with the good interlaminar shear and across-ply tension strengths that are so important in nozzle components.

Among carbonizable fiber precursors, aerospace rayon is not a particularly strong fiber, and carbonized or graphitized rayon is also not particularly strong. However, fiber strength in itself is not a determining factor for nozzle applications. Strength only has to accommodate the stress generated during motor operation. Stress originates from two sources: gas pressure and thermal expansion of the insulator. The actual stress developed depends on the elastic modulus of the material. Rayon-based fabric reinforcements have relatively low values of elastic modulus; therefore they develop low stress. When properly designed and fabricated, rayon-based fabric reinforcements in composite insulators have adequate strength to accommodate these stresses.

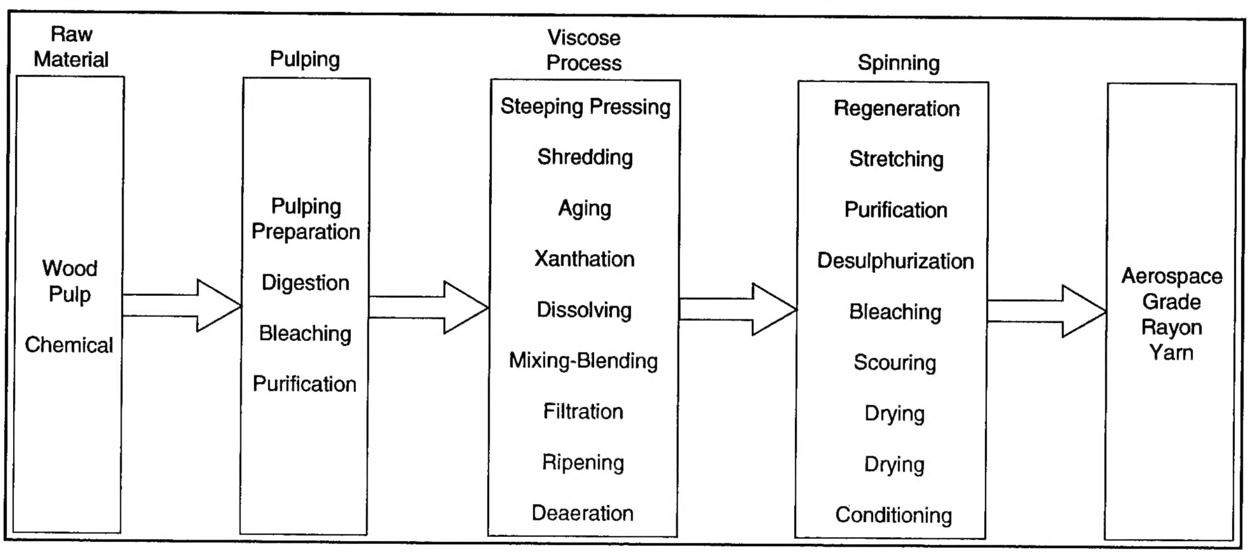

Figure 1. Viscose Process Overview[2]

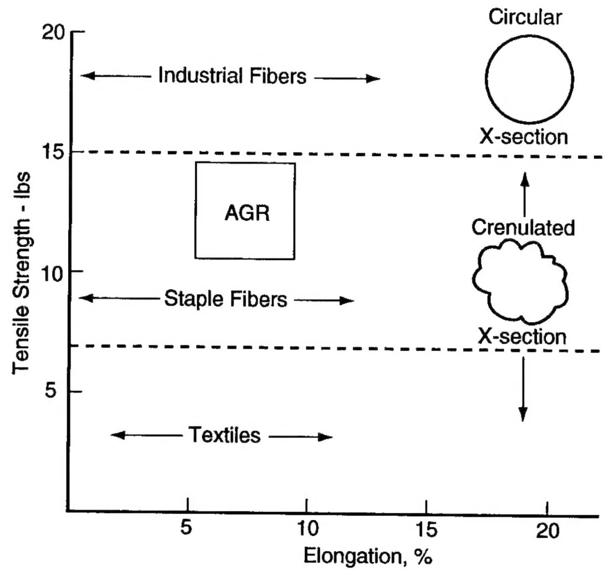

Figure 2. Rayon Yarn Property Variability[3]

RAYON MANUFACTURE AND ITS PRODUCTS

Rayon fibers are made by the same processes as other synthetic fibers. In the spinning operation, the rayon viscose is drawn through a spinneret that contains multiple fine holes, each hole creating an individual filament. The filaments are then dried, pulled together, and twisted to make a yarn. The aerospace grade rayon has used two yarn sizes, a 1650 denier with 720 filament count, and a 1100 denier with 490 filament count. These yarns are woven into fabric of three types of weave construction: 8 harness satin weave, 5 harness satin weave, and plain weave. The white broad goods are thermally converted into black goods at three temperature ranges: low, intermediate, and high fired (Figure 3). The black goods from the low and intermediate conversion process are referred to as carbon cloth; the high-fired product is graphite cloth. Table 2 lists some selected properties for these products; except for purity levels, there is not a great deal of difference among them. A significant property difference not shown here is that graphite fabric reinforced nozzle components will show about 50% more erosion resistance then carbon fabric reinforced parts. For this reason graphite fabric reinforcement is used in regions of a nozzle having higher erosion exposure.

Rayon Yarn	Weave (White Goods)	Carbon/Graphite Conversion (Black Goods)
1650 Denier/ 720 Filament Count	8 Harness Satin Weave Single Ply	Low Fired <1400°C
1100 Denier/ 490 Filament Count	5 Harness Satin Weave 2 Ply	Intermediate Fired 1600-1700°C
	Plain Weave 3 Ply	High Fired ~2500°C

Figure 3. Process Flow for Conversion of Rayon Yarn into Reinforcing Fabric

Table 2. Selected Properties of Converted Rayon Fibers[2, 4]

Fiber Property	Low Fired	Intermediate Fired	High Fired
Fiber Density, g/cc	1.46-1.53	1.46-1.50	1.44-1.45
Tensile Strength, Ksi	~100	~100	~100
Tensile Modulus, Msi	~6	~6	~6
Carbon Assay, wt%	96+	99+	99.9
Ash Content, wt%	0.4	0.3	0.01
Theremal Conductivity, W/mK	3.7	4.0	4.1
Surface Aera, m^2/g	4.0	6.0	3.0

RAYON-BASED CARBON FABRIC USED IN NOZZLES

Nozzle insulators are composite materials reinforced with rayon-based carbon fabric in a phenolic resin matrix. Over the years, several composite constructions have been used. The involute design is a hand-lay-up method for constructing a component from shaped pieces of fabric, pre-impregnated with resin (prepreg) so that one edge of the fabric terminates at the inside diameter of the part, the other terminates at the outside diameter. The layed-up fabric makes a small angle with the tangent to the part. This is a costly and time-consuming method of construction and is no longer used. Molding compounds consist of chopped (1/2" x 1/2") fabric mixed with pulverized resin and formed in a mold. A straight tape wrapped part uses strips of prepreg wrapped over a male mandrel. Although most nozzle components are conical in shape, this method is constrained in that the wrap must always be parallel to the conical axis.

The method that has nearly replaced all others is the bias-tape wrap. This method uses strips of prepreg cut on the bias and sewn together at the ends to make a continuous bias tape that can be wrapped without buckling on either a male or female mandrel at an angle to the axis. This method is machine operated and provides the component with superior thermal and structural properties relative to the other methods.

In every case, a formed part must be cured. For molded parts, temperature and pressure are applied while the part

is in the mold. Unmolded parts are vacuum bagged and placed in either a hydroclave or autoclave where temperature and pressure can be applied. Cured parts are then machined by either diamond grinding or single point machining. Figure 4 summarizes the manufacturing processes for nozzle components.

Phenolic composites reinforced with rayon-based carbon fabric are universally used in modern solid rocket nozzle manufacture. Figure 5 shows a typical design of a large, modern SRM nozzle with the rayon-based carbon/phenolic components identified. Note that all flame surfaces are protected with these materials and that rayon-based graphite reinforcement is used in regions of high erosion (throat and entrance components). The primary requirement of these components is to provide thermal protection to the metal structures that support them and that transfer thrust loads. Typical design requirements are such that during a nominal motor firing, these metals structures are to experience minimal temperature rise at the end of motor burn.

Process	Description	Parameters
Rayon Yarn Manufacturing	Spinning/ Drawing	Denier (g/9000M) 1650/1100 Count (filament/tow) 750/490
Fabric Manufacture	Weaving of Broadgoods	5 Harness satin 8 Harness satin Plain weave
Carbonization/ Graphitization	Converts "white goods" to "black goods"	Temperature: <1400°C, 1600-1700°C, ~2500°C
Prepreg	Impregnate fabric with resin	Resin, filer, reinforcement Composition range of constituents
Composite Fabricators	Converts prepreg in composite billet	Lay-up orientation Hydroclave/autoclave/ mold press Temperature/pressure
Component Machining	Machine to print	Single point machining/ diamond grinding

Figure 4. Manufacturing Processes for Rayon-Based Composites

ALTERNATIVES TO RAYON

Two commercially available alternative carbonizable fibers are made from either polyacrylonitrile or pitch (oil or coal base).[6] PAN-based carbon fibers are widely used in sporting goods and as reinforcement in light-weight structural composites in aerospace applications. PAN is wet-spun using a suitable solvent, dried, stretched, air stabilized at 430°F, and carbonized in the 1600-1700°C range. Compared to rayon-based carbon, these fibers exhibit high strength, stiffness, and thermal conductivity. The PAN fibers are spun circular, but when carbonized become slightly oval or kidney-bean shaped. When used with

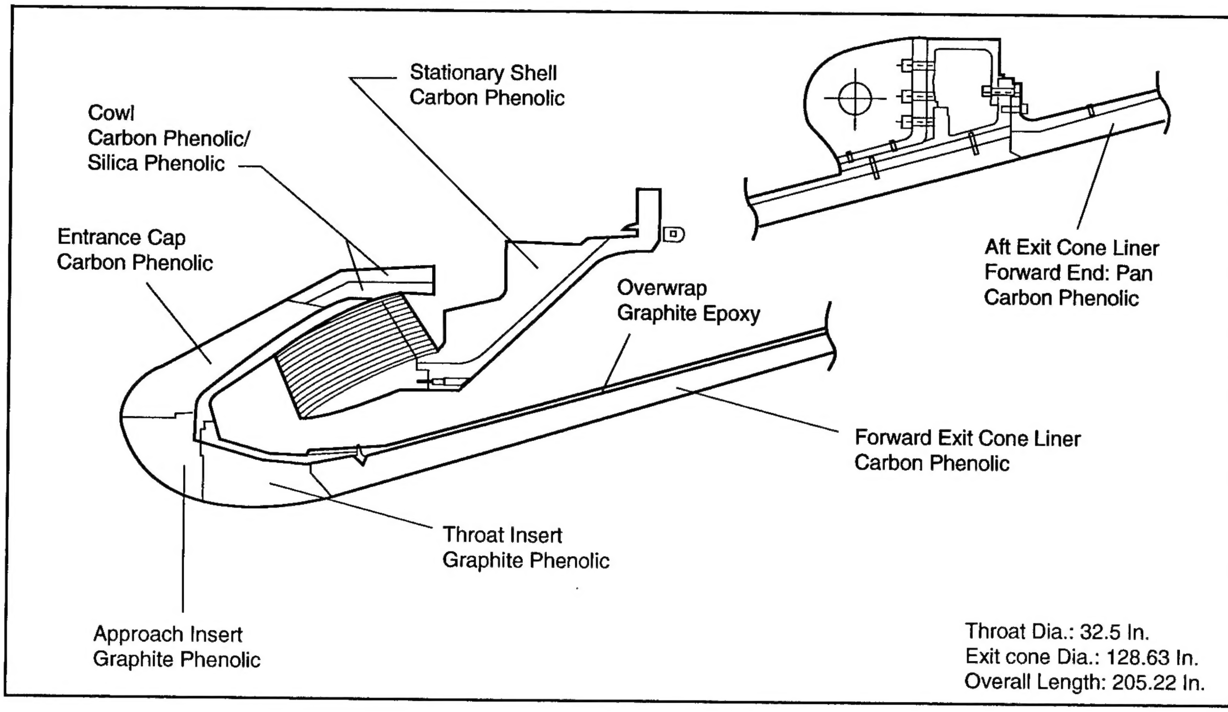

Figure 5. Cross Section of Typical Motor Nozzle[5]

phenolic resin, the interface between fiber and matrix develops about one-half the strength of rayon-based carbon fibers and phenolic resin.

Pitch fibers are hot-melt spun, carbonized, and stress-graphitized at very high temperatures. Pitch-based carbon fibers are circular, but after graphitization become axially split so that in cross-section they appear like a pie with a missing piece. These fibers are of interest commercially because of their very high stiffness and very high thermal conductivity. When evaluated in test motors, the high conductivity of pitch-based carbon created excessively deep char-depths; they do not represent a serious alternative to rayon-based carbon in nozzle components.

PAN-based carbon fibers, however, have been evaluated as alternative reinforcement for nozzle insulators for more than 15 years with both NASA and Air Force funding, and currently with Navy funding. Thermal conductivity, a critical performance property, was found to be adjustable by varying the carbonization temperature. A comparison of thermal conductivity for various carbon fibers is shown in Figure 6. By dropping carbonization temperature below 1400°C, PAN-based carbon fiber conductivity values can be reduced to about one-half of standard PAN-based fibers, but are still two to three times the value of rayon-based carbon.

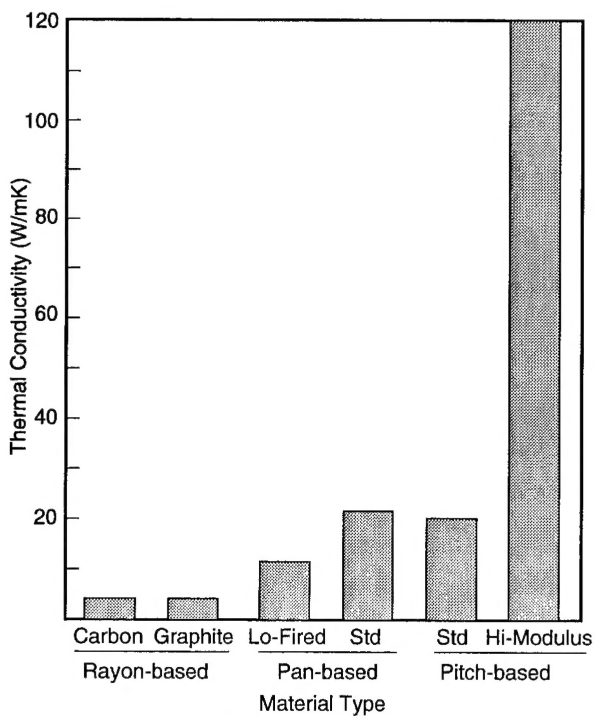

Figure 6. Thermal Conductivity of Various Carbon Fibers[7]

Small rocket motor tests that compared low-fired PAN-based carbon reinforcement with rayon-based carbon reinforcement show nearly comparable performance in char and erosion rates, as presented in Table 3. When large motors were evaluated, the low-fired PAN-based carbons showed deeper char penetration, similar to standard-fired PAN. Post test analysis has shown that in longer motor firings, the advancing heat travels along the fiber length, converting the fiber into the high conductivity, high-fired fiber. Additionally, other problems were uncovered with large motors. In one case, a Brutus motor experienced a nozzle burn-through attributable to delamination or pocketing and subsequential thermal penetration. A Delta II nozzle with PAN-based carbon components experienced an unbond/delamination event 0.1 sec into burn that allowed anomalous gas flow and heat penetration in and around the mating insulator components.[9]

Table 3. Nozzle Performance Comparisons for Various Materials[8]

Composite Material Type	Approximate Fiber Process Temperature (°C)	Normalized Erosion Rate (mil/sec)	Char Depth (mil)
Rayon-based carbon	1330	8.2	390
Rayon-based graphite	2500	6.4	370
Low-fired PAN	1350	6.8	420
Standard PAN	1650	6.3	530
High-fired PAN	2400	4.9	820

Material characterization of PAN-based carbon phenolic materials shows that the propensity for delamination is a consequence of weak fiber-matrix bonding that reduces across-ply strength and interlaminar shear strength. These values are typically one-half of those for rayon-based carbon phenolic materials. Structural analyses indicate that, for large motor nozzle designs based on rayon-based carbon experience, the structural margin to prevent delamination for PAN-based carbon is either very small or negative.

The body of data and experience assembled to evaluate PAN-based carbon reinforcement to replace rayon-based carbon reinforcement in present nozzle designs has shown that PAN-based carbon reinforcement has:

- Higher thermal conductivity which reduces thermal margins
- Lower across-ply strength, which reduces structural margins for delaminations

- Higher density, which adds weight
- Higher stiffness, which increases bondline stresses

Recent work funded by NASA in an attempt to overcome some of the performance problems by reducing the resin content in the composite was unfortunately canceled before the effect could be demonstrated.

PRESENT STATUS

Following the NARC announcement of its planned closure, on 29 May, an industry-wide meeting was held in Salt Lake City to discuss the implication of the impending shutdown and to explore alternative options. One consequence of the meeting was the placement of orders sufficient to satisfy near and intermediate-term requirements for most major programs. Equally important is the vendor's commitment to fill these orders prior to shutdown. A second meeting was held on 7 August to review status and further explore options. One of these options is selection and qualification of foreign sources. Two foreign rayon yarn manufacturers presented their capabilities at the meeting.

In the interim between these meetings, a joint DoD and NASA team was assembled under the title "Space Launch and Missile Propulsion Systems Industrial Capabilities Working Group of the Aeronautics and Astronautics Coordinating Board." On 8 August, technical subgroups met to address the following specific issues raised by the events.

- Determine the feasibility of promulgating a common fiber specification/qualification requirement.
- Examine advanced materials technology for near term (three to five years) alternative replacement material.
- Establish the validity of extended rayon storage life.
- Evaluate the capability of alternative rayon fiber suppliers to meet NASA/DoD requirements. (Included option to continue NARC production for uncommitted inventory.)

Each subgroup has prepared a report that has been integrated into a single study. The integrated report has been presented without recommendations to the Acquisition Directorates of both NASA and DoD for further study and consideration. At this time it is too early to expect a position. However, the sequence of events leading to the present is noteworthy in the following aspects:

- Cooperation between NASA and DoD to establish a common position.
- Industry's response to protect active programs that also buys time to permit thoughtful consideration of the options.
- Joint government/industry concern for minimizing the cost and establishing long-term rayon yarn availability.
- High-level visibility of rayon's unique set of properties and its vulnerability in the world's market place.
- Accentuation of the need to re-activate materials development to qualify alternative replacement materials.

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